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AUTHOR(S):

Nakahara, Masaru; Osugi, Jiro

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## ON IONIC ACTIVITY COEFFICIENTS AT HIGH PRESSURE

BY MASARU NAKAHARA AND JIRO OSUGI

A more general formula than Eq. (3) in the previous paper<sup>1)</sup> has been obtained from the Debye-Hückel equation to calculate the activity coefficients of ions at high pressure. This equation shows that the magnitudes of the pressure effect on the mean activity coefficient depend very slightly on the concentration (molality). The limiting equation (Eq. (3) in Ref. (1)) has been proved to be valid within 1% error up to  $m \approx 0.1$  even at 10 kbar. Some other formulas proposed until now for the same purpose are also discussed.

## Introduction

Since at present we have no direct experimental data on the ionic activity coefficients at high pressures, it is not easy to determine which formula is the best one for their estimation. However, the validity<sup>2)</sup> of the Debye-Hückel-Onsager equation of conductivity at high pressures seems to indicate the applicability of the limiting Debye-Hückel equation to the activity coefficients of ions in dilute solutions at high pressure. Along this line the limiting equation (Eq. (3) in Ref. (1)),

$$\log \gamma^{(p)} / \log \gamma^{(1)} = (\rho^{(p)} / \rho^{(1)})^{1/2} (D^{(1)} / D^{(p)})^{3/2} \equiv L^{(p)} \quad (1)$$

was obtained and compared with Hamann and Linton's empirical equation (Eq. (5) in Ref. (1)),

$$\log \gamma^{(p)} / \log \gamma^{(1)} = 1 + \frac{F(P-1)}{1+b(P-1)} \equiv H-Li^{(p)} \quad (2)$$

At that time the numerical mistake was made in the calculation of  $H-Li^{(p)}$  as already corrected by the authors<sup>3)</sup>; the deviation of  $H-Li^{(p)}$  from  $L^{(p)}$  is considerably small just as declared in Hamann's comment<sup>4)</sup>. However, the main point of our criticism was the absence of any reason why  $H-Li^{(p)}$  could represent the pressure dependence of the free energy of ion-ion interaction. The numerical reproducibility only can not be any theoretical justification, especially because  $H-Li^{(p)}$  is adjusted to  $L^{(p)}$  around 1 bar by virtue of  $F$  in Eq. (2). As shown in Table I, for example, Linton's empirical formula<sup>5)</sup>,

$$Li^{(p)} = 1 - \frac{4.803 \times 10^{-5}(P-1)}{[1 + 2 \times 10^{-4}(P-1)]^{1/2}} \quad (3)$$

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1) M. Nakahara and J. Osugi, *This Journal*, **45**, 69 (1975)

2) M. Nakahara, K. Shimizu and J. Osugi, *ibid.*, **42**, 12 (1972)

3) M. Nakahara and J. Osugi, *ibid.*, **46**, 56 (1976)

4) S. D. Hamann, *ibid.*, **46**, 95 (1976)

5) Private communication from Max Linton to M. N., April 28, 1976

where  $4.803 \times 10^{-5}$  is used as in Ref. (4) for  $F$  at  $25^\circ\text{C}$  in water instead of  $4.83 \times 10^{-5}$  in Ref. (1), is more closely similar to  $L(\rho)$  in the numerical sense. Concerning the above main point, the authors sent a letter to El'yanov and after a few months got an answer from him<sup>6)</sup> in which he for the first time succeeded in deriving  $H-Li(\rho)$  as an approximate form of Eq. (1). Thus  $H-Li(\rho)$  has now such a theoretical background that it may be safely used for the estimation of ionic activity coefficients. But at least those who have a portable electronic functional calculator may feel that  $L(\rho)$  is more convenient and accurate than  $H-Li(\rho)$  for the estimation of ionic activity coefficients in a certain solvent at a certain temperature at high pressures, because not only  $F$  but also  $b$  in Eq. (2) may depend on temperature and solvent<sup>7)</sup>. In spite of his great contribution, El'yanov's opinion appearing above and below Eq. (c) in Ref. (6) can not be approved of in view of the basic nature of the Debye-Hückel theory. Some cancellation of ion-water-interaction terms occurs in the right-hand side of Eq. (c). In Eqs. (1) and (2) is taken into account only the variation of ion-ion interaction with pressure, as can be understood from the below analysis.

#### Comparison of several formulas

For many 1:1 electrolytes in aqueous solution (the density,  $\rho$ : the dielectric constant,  $D$ ) at 1 bar the Debye-Hückel equation,

$$\log \gamma_{\pm} = \log \sqrt{\gamma_{+}\gamma_{-}} = -A\sqrt{m}/(1+Bd\sqrt{m}), \quad (4)$$

where

$$A = 1.825 \times 10^6 (\rho)^{1/2} (DT)^{-3/2}, \quad (5)$$

$$B = 50.29 (\rho)^{1/2} (DT)^{-1/2}, \quad (6)$$

and  $d$  is the average closest-approach distance (an adjustable parameter) in  $\text{\AA}$  of ions involved, is capable of representing the observed mean activity coefficients up to  $m \approx 0.1$ . In the right-hand side of Eq. (4) the numerator reflects the long-range interionic interaction and the second term in the denominator the short-range interionic interaction which becomes important at higher concentrations. While in a broad sense the ion-water interaction is implied through  $d$  in Eq. (4), a linear (empirical) term  $b'm$  is usually added to the right-hand side of Eq. (4) so as to involve the ion-water interaction explicitly. If the functional form of Eq. (4) is invariant to the application of high pressure, we may have

$$\log \gamma_{\pm}(\rho)/\log \gamma_{\pm}(1) = L(\rho)(1+B'd(1)\sqrt{\rho(1)/D(1)}\sqrt{m})/(1+B'd(\rho)\sqrt{\rho(\rho)/D(\rho)}\sqrt{m}), \quad (7)$$

where  $B'$  is a constant ( $=2.912$  at  $25^\circ\text{C}$ ) defined by the equation,

$$B' = B/(\rho^{1/2}D^{1/2}) = 50.29/T^{1/2}. \quad (8)$$

In case  $m \leq 0.1$ , the second term in the denominator of the right-hand side of Eq. (7) is usually less than

6) Private communication to J. O. (July 28, 1976) which is published according to our advice; B. S. El'yanov, *This Journal*, **46**, 96 (1976)

7) M. Nakahara, *ibid.*, **44**, 57 (1974)

unity. Consequently Eq. (7) can be expanded as the power series with respect to  $\sqrt{m}$ :

$$\log \gamma_{\pm}^{(p)} / \log \gamma_{\pm}^{(1)} = L^{(p)} [1 + B' d^{(1)} \sqrt{\rho^{(1)} / D^{(1)}} (1 - a_r \sqrt{\rho_r / D_r}) \sqrt{m} + (B' d^{(1)} \sqrt{\rho^{(1)} / D^{(1)}})^2 a_r \{- \sqrt{\rho_r / D_r} + a_r (\rho_r / D_r)\} m + (\quad) m^{3/2} + (\quad) m^2 + \dots], \quad (9)$$

where  $a_r = d^{(p)} / d^{(1)}$ ,  $\rho_r = \rho^{(p)} / \rho^{(1)}$  and  $D_r = D^{(p)} / D^{(1)}$ . When  $a_r = 1$  and  $m \leq 0.1$ , Eq. (9) may be truncated as follows:

$$\begin{aligned} \log \gamma_{\pm}^{(p)} / \log \gamma_{\pm}^{(1)} &= L^{(p)} [1 + M(1 - r^{(p)}) \sqrt{m} - M^2 r^{(p)} (1 - r^{(p)}) m] \\ &= L^{(p)} [1 + M(1 - r^{(p)}) \sqrt{m} (1 - M r^{(p)} \sqrt{m})] \equiv N - O^{(p)}, \end{aligned} \quad (10)$$

where

$$M = 50.29 T^{-1/2} d^{(1)} \sqrt{\rho^{(1)} / D^{(1)}}, \quad (11)$$

and

$$r^{(p)} = \sqrt{\rho_r / D_r}. \quad (12)$$

The magnitudes of  $N - O^{(p)} / L^{(p)}$  at  $m = 0.1$  at 25°C have been calculated by using the physical properties of water at high pressures and listed in Table 1 for comparison. The significance of the

Table 1 The values of  $\log \gamma_{\pm}^{(p)} / \log \gamma_{\pm}^{(1)}$  in water at 25°C at various pressures

Pressure/kbar	0.5	1	2	3	4	5	6	8	10
$L^{(p) a)}$	0.9770	0.9560	0.9180	0.8846	0.8549	0.8281	0.8038	0.7611	0.7237
$L^{(p) b)}$	0.9779	0.9569	0.9188	0.8860	0.8569	0.8318			
$(L^{(p) b}) / L^{(p) a} - 1) \times 10^3$	0.92	0.94	0.87	1.6	2.3	4.5			
$(N - O^{(p) c}) / L^{(p) a} - 1) \times 10^3$	0.15	0.40	1.1	1.9	2.9	3.8	4.8	6.9	8.9
$(H - Li^{(p)} / L^{(p) a} - 1) \times 10^3$	0.00	0.00	0.98	2.8	5.4	8.9	13	23	36
$(Li^{(p)} / L^{(p) a} - 1) \times 10^3$	0.10	0.21	0.87	1.7	2.2	2.5	2.4	0.79	-1.4

\* In all cases the density data are taken from Ref. (8).

a) The values of  $D^{(p)}$  up to 5kbar are from Ref. (9) and those at 6, 8 and 10kbar from Ref. (10).

b) The values of  $D^{(p)}$  are from Ref. (11).

c)  $m = 0.1$ ;  $d^{(1)} = 5 \text{ \AA}$ ;  $M = 1.66$ ;  $D^{(p)}$  up to 5kbar from Ref. (9) and at 6, 8 and 10kbar from Ref. (10).

equation,  $N - O^{(p)}$  may be summarized as follows: 1)  $L^{(p)}$  can be approached in a natural manner in the limit of infinite dilution; 2)  $N - O^{(p)} / L^{(p)}$  depends very slightly on the molality; 3)  $L^{(p)}$  can be utilized practically with a sufficient accuracy in many ionic systems at considerably high concentrations; 4)  $L^{(p)}$  and presumably  $H - Li^{(p)}$  reflect only changes of the ion-ion interaction with pressure by means of the physical properties of the solvent.

An early and different attempt to calculate the activity coefficients of ions at high pressure from those at 1 bar was described by Harned and Owen<sup>12)</sup>. The thermodynamic equation,

8) T. Grindley and J. E. Lind, *J. Chem. Phys.*, **54**, 3983 (1971)

9) K. S. Srinivasan and R. L. Kay, *ibid.*, **60**, 3645 (1974)

10) W. L. Lees, Dissertation, Harvard University (1941)

11) L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65**, 2906 (1969)

12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Chap. (12), Sec. (4), Reinhold (1958)

$$(\partial \ln \gamma_{\pm} / \partial P)_{T, m} = (\bar{V} - \bar{V}^{\circ}) / \nu RT, \quad (13)$$

where  $\nu=2$  for 1:1 electrolytes, is integrated with respect to pressure by assuming the partial molal compressibilities at 1 bar,  $\bar{\kappa}$  and  $\bar{\kappa}^{\circ}$  to be constant over a small pressure range;  $\bar{V} - \bar{V}^{\circ} = (\bar{V} - \bar{V}^{\circ})^{(1)} - (P-1)(\bar{\kappa} - \bar{\kappa}^{\circ})^{(1)}$ . The limiting Debye-Hückel equations,

$$(\bar{V} - \bar{V}^{\circ})^{(1)} = 1.5 S_v^{(1)} \sqrt{\rho^{(1)} m} \quad (14)$$

and

$$(\bar{\kappa} - \bar{\kappa}^{\circ})^{(1)} = 1.5 S_{\kappa}^{(1)} \sqrt{\rho^{(1)} m} \quad (15)$$

are inserted into the integrated form of Eq. (13): finally they have obtained

$$\begin{aligned} \log \gamma_{\pm}^{(p)} / \log \gamma_{\pm}^{(1)} = & 1 + [1.332 \times 10^{-5} S_v^{(1)} (P-1) \\ & - 0.666 \times 10^{-5} S_{\kappa}^{(1)} (P-1)^2] \sqrt{\rho^{(1)} m} / \log \gamma_{\pm}^{(1)}. \end{aligned} \quad (16)$$

The magnitudes of the pressure effect upon the activity coefficients of HCl, KCl, NaCl and NaOH at 1 molarity are computed up to 1 kbar and tabulated in their book<sup>12)</sup>, though the upper limit of the validity of Eqs. (14) and (15) would be far lower than 1 molarity. As shown in Table 2, the mean

Table 2 The values of  $\log \gamma_{\pm}^{(p)} / \log \gamma_{\pm}^{(1)}$  of NaCl in water at 25°C at high pressures calculated by Eq. (16)

$P/\text{kbar}$	$m$	$L^{(p)}$	$10^{-3}$	0.1	1
0.5		0.977	0.975	0.963	0.932
1		0.956	0.957	0.938	0.885

a) From the second row in Table 1.

activity coefficients of NaCl in water at 25°C estimated by using Eq. (16) and the literature values<sup>13)</sup> of  $\log \gamma_{\pm}^{(1)}$  reproduce approximately the limiting values,  $L^{(p)}$  at  $m=10^{-3}$  but do not at  $m=1$ ; it might be a natural result in consideration of the suppositions used during the derivation of Eq. (16). Thus Eq. (16) depends on the concentration more strongly than  $N-O^{(p)}$ . An inherent defect of Eq. (16) would be that it is parabolic with respect to pressure. The value of  $\log \gamma_{\pm}^{(p)}$  has a minimum at  $P = S_v^{(1)} / S_{\kappa}^{(1)} + 1$ ;  $P \approx 2780, 1880, 1890$  and  $2000$  bar for HCl, KCl, NaCl and NaOH in water at 25°C, respectively.

The contribution of the activity coefficient of i-ion to the reaction or activation volumes in water at 25°C may be estimated approximately by using Eq. (2) and the limiting Debye-Hückel equation,

$$\log \gamma_i^{(1)} = -0.509 z_i^2 \sqrt{I},$$

where  $I$  is the ionic strength in molality, as follows:

$$\begin{aligned} \Delta \bar{V}_i / (\text{cm}^3 \text{mol}^{-1}) \text{ at 1 bar} \\ = RT (\partial \ln \gamma_i^{(p)} / \partial P)_{T, m} \end{aligned}$$

13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Chap. 9, Butterworths (1968)

$$\begin{aligned}
 &\simeq FRT \ln \gamma_i^{(1)} \\
 &\simeq 1.40 z_i^2 \sqrt{I} \quad (0.44 z_i^2 \text{ at } I=0.1). \quad (17)
 \end{aligned}$$

As can be seen in Eq. (17), the magnitude of  $\Delta \bar{V}_i$  is small when the ionic strength is low, but may be considerably large when the ionic valence is high; practically the difference in  $\Sigma z_i^2$  between reactants and products (or transition state) is important.

*Laboratory of Physical Chemistry  
Department of Chemistry  
Faculty of Science  
Kyoto University  
Kyoto 606  
Japan*